CHAPTER 1

INTRODUCTION

1.1 Naphtha Reforming

Naphtha is a complex mixture of C_5 to C_{12} hydrocarbons in the boiling point range from 90 °C – 180 °C [1]. Catalytic reforming is extensively practiced in the petroleum-refining industry to rearrange the hydrocarbon molecules in the naphtha feedstock to produce higher octane number components such as isomers, naphthenes and aromatics. These high octane components are blended with naphtha to produce gasoline reformate with the necessary octane number. Aromatics are also needed for further processing to petrochemicals. Hydrogen is a by-product useful for other refining processes such as hydro-treating and hydro-cracking. The unit process reactions in reforming process include dehydrogenation and aromatization.

$$\textit{Paraffins (P)} \rightleftharpoons \textit{Naphthenes (N)} + H_2 \quad (1.1)$$

$$\textit{Naphthenes (N)} \rightleftharpoons \textit{Aromatics (A)} + H_2 \quad (1.2)$$

These reactions are reversible and endothermic in nature. Thermodynamically high temperature and low pressure favor these reactions. Some of the hydrogen is recycled to sustain reformer reactor pressure and to restrain coke formation.

Naphtha reforming needs a dual-function of catalyst with metal and acid catalyst functions. The metal (Pt or Pt-Re or Pt-Ir) is dispersed on alumina which has some acidity. Addition of chlorine to alumina enhances its acidity. The metal catalyst promotes dehydrogenation (extraction of hydrogen from hydrocarbons) and aromatization reactions while the acid catalyst promotes cracking reactions. Reforming reactions require a delicate balance between these metals and acid sites. Chlorinated alumina with Pt/Re is widely used as the catalyst.

Catalytic naphtha reforming processes are accompanied by side reactions such as hydro-cracking of naphtha which can consume hydrogen and produce lighter hydrocarbon molecules with carbonaceous deposits causing catalyst deactivation.

$$Naphthenes\ (N) + (n/3)H_2 \rightarrow Light\ Gas\ (LG) + C \downarrow \tag{1-3}$$

$$Paraffins\ (P) + \left(\frac{n-3}{3}\right)H_2 \rightarrow Light\ Gas\ (LG) + C \downarrow \tag{1-4}$$

Where *n* is carbon number and C ↓ is coke deposition on the catalyst. These reactions are irreversible and exothermic in nature.

1.2 Naphtha Reforming Technology

Reforming is a net endothermic vapor phase reaction in presence of a slowly deactivating solid phase catalyst. Adiabatic packed bed reactors are used to carry out reforming process. There are three types of reforming process technologies - Semi Regenerative Reforming (SRR), Fully Regenerative Reforming (FRR) and Continuous Regenerative Reforming (CRR).

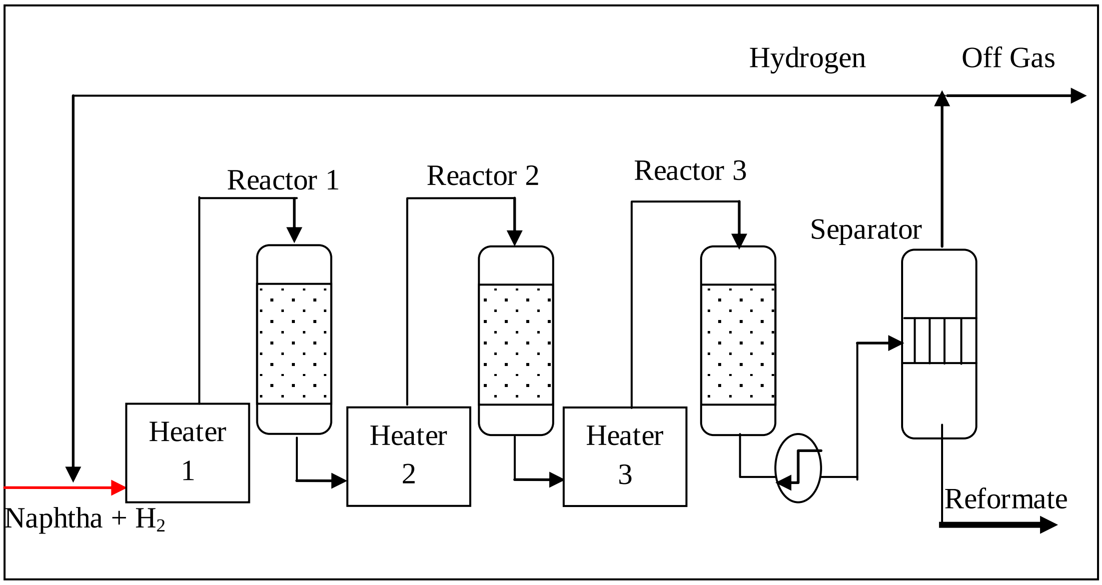

Fig. 1.1: Semi Regenerative Reforming (SRR) technology.

Fig. 1.1 shows the SRR technology. The SRR unit consists of three adiabatic fixed bed reactors in series with facility to pre- heat the feed to each unit. Early SRR units were operated at relatively high pressure (25 – 35 bars). The developments of improved catalysts that had lower tendency for coke formation enabled operation at lower pressure (15-20 bars), while maintaining same catalyst life (typically 1 year). The longer the required cycle length, the greater the amount of catalyst. The reformers are shut down periodically (typically six months) as catalyst activity declines because of coke deposition to regenerate the catalysts in situ by controlled coke burn off [2], [3]. The catalyst is also treated with chlorine in order to replenish acid sites of the catalyst.

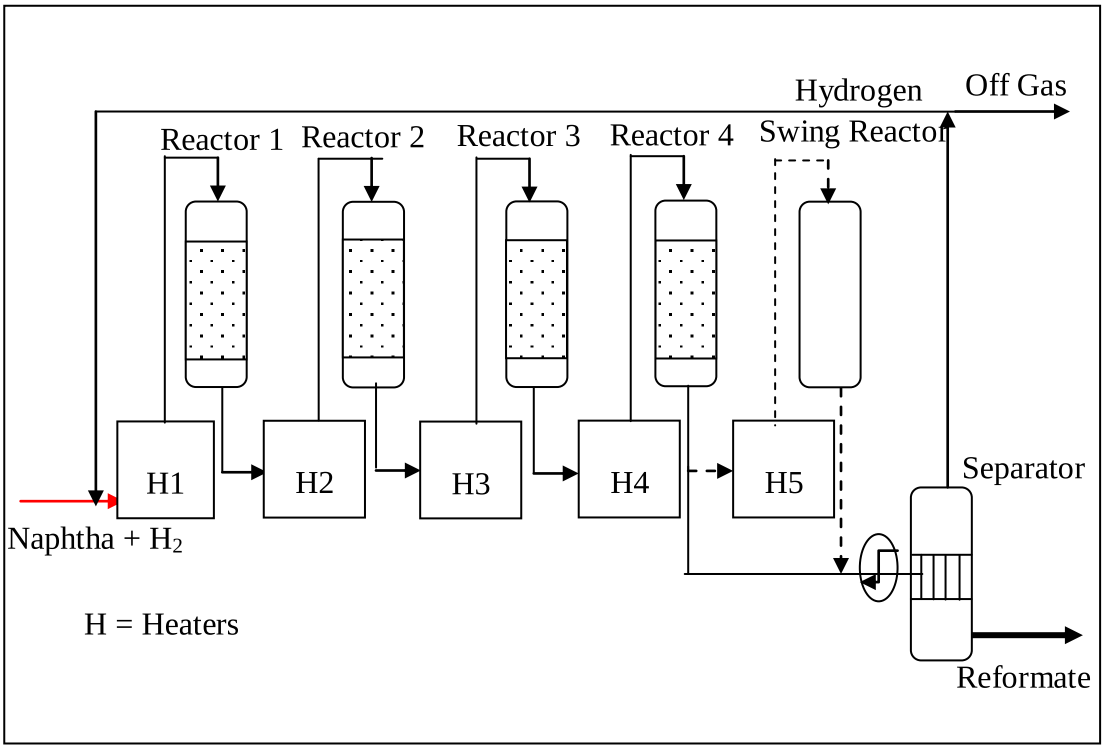

Fig. 1.2: Fully Regenerative Reforming (FRR) technology.

In Fully Regenerative Reforming (FRR) process technology shown in Fig. 1.2, an additional swing reactor is provided to allow one reactor to be taken off line at a time for regeneration while the rest of the reactors permit continuous production. Generally, the reactors are at the same size. FRR is able to operate without shutdown for two or three year [1] - [2].

Continuous Regenerative Reforming unit (CRR) developed by UOP and IFP is widely used in the industry and shown in Fig.1.3. It consists of a reformer and a regenerator. The reformer consists of four reactors, stacked one on top of the other and the catalyst particles move as a moving bed through the stack of four reactors from top to bottom while the reactant flows radially [1], [3]. Such reactors are known as radial flow moving bed reactors (RMFBR).

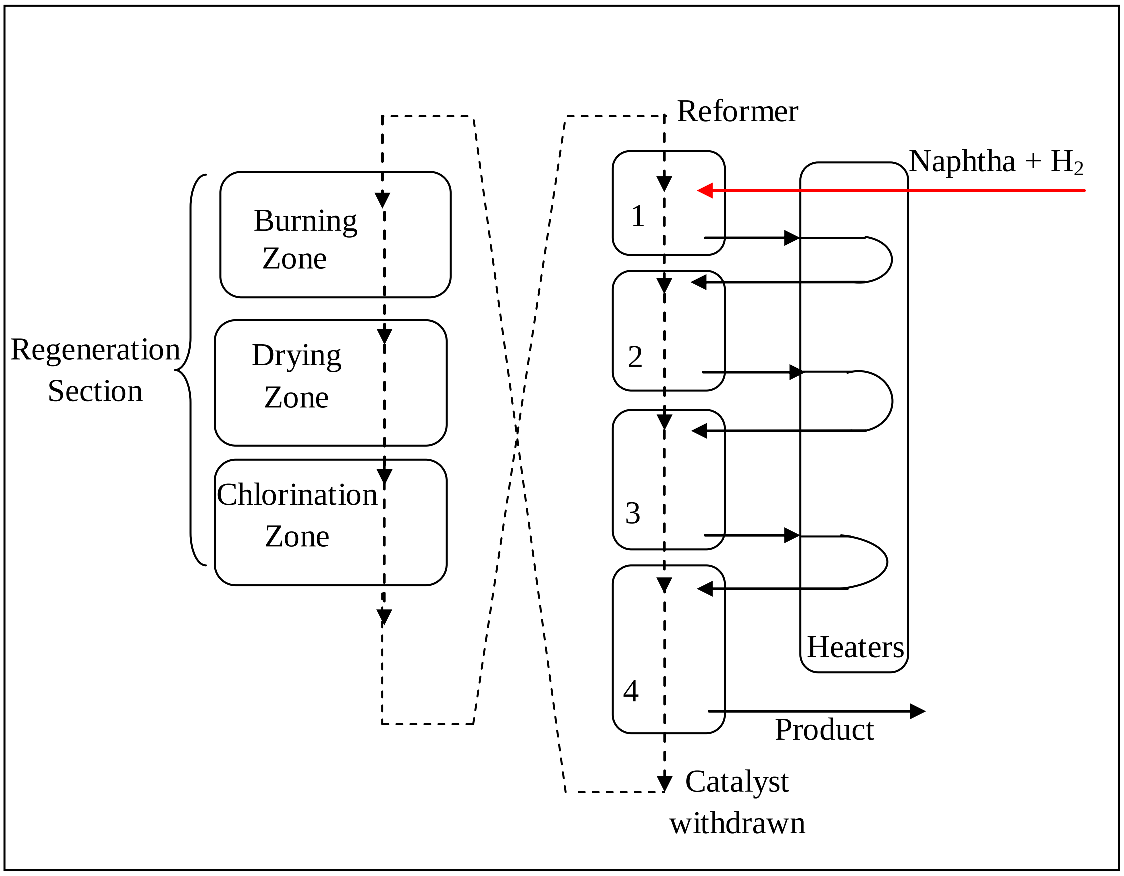

Fig. 1.3: Continuous Regenerative Reforming unit (CRR) with radial flow moving bed reactor.

Coked catalyst is continuously withdrawn from the bottom reactor and sent to the top of regeneration reactor; the catalyst moves downwards as a moving bed while they get regenerated by controlled coke burn off, get dried and chlorinated. Movement of catalyst particles generates fines due to attrition; the fines are removed and replenished with fresh catalyst while returning the fresh catalyst to the top of the first reforming reactor for continuous basis. Catalyst transports through the reactors and the regenerator is driven by gravitational force, whereas gas lift will transport the catalyst from the reactor/regenerator bottom to the top of the regenerator/reactor.

Catalyst circulation rate is controlled to maintain the reformate yield. The continuous reforming process is capable of operation at lower pressures and higher temperatures as the catalyst activity is maintained high by the continuous regeneration of the catalyst on catalyst circulation.

In CRR unit, naphtha gas is mixed with hydrogen and gets heated to the reaction temperature before it enters the first reactor. The effluent from the first reactor will reheat to reaction temperature before enters the second reactor and the effluent from second reactor get reheat before enters the third reactor. Effluent of third reactor gets reheat and enters the fourth reactor. Effluent from fourth reactor goes to separator to separate reformate, light gas and hydrogen.

1.3 Naphtha Reforming in Radial Flow Moving Bed Reactor

Generally the four reactors are quite tall and hence the pressure drop for such tall reactors can be excessively high. However, organizing the gas flow in the radial direction can decrease velocity as well as path length for flow and hence can reduce the pressure drop drastically. In radial flow reactors, the catalyst is held as an annular bed between two perforated coaxial cylinders; the reactant gas flow can be from outside to inside (or inside to outside) through the moving bed in the annular space in between the two coaxial perforated cylinders [4]. The packed bed of particles can move downwards to facilitate withdrawal of slowly decaying catalysts. Such beds are known as a radial flow moving bed reactor (RFMBR) as shown in Fig. 1.4.

A RFMBR is used in UOP/ IFP for reforming as well as catalyst regeneration by controlled coke burn off, drying and chlorination. The catalyst circulation rate is low as the catalyst decays in weeks. In contrast, catalyst circulation rates in FCC reactors are very high as the catalyst decays in seconds.

Thus, RFMBR is a unique energy efficient reactor used for naphtha reforming and dehydrogenation of propane. Though they are widely used in petroleum refineries, very little has been published about them in the open literature.

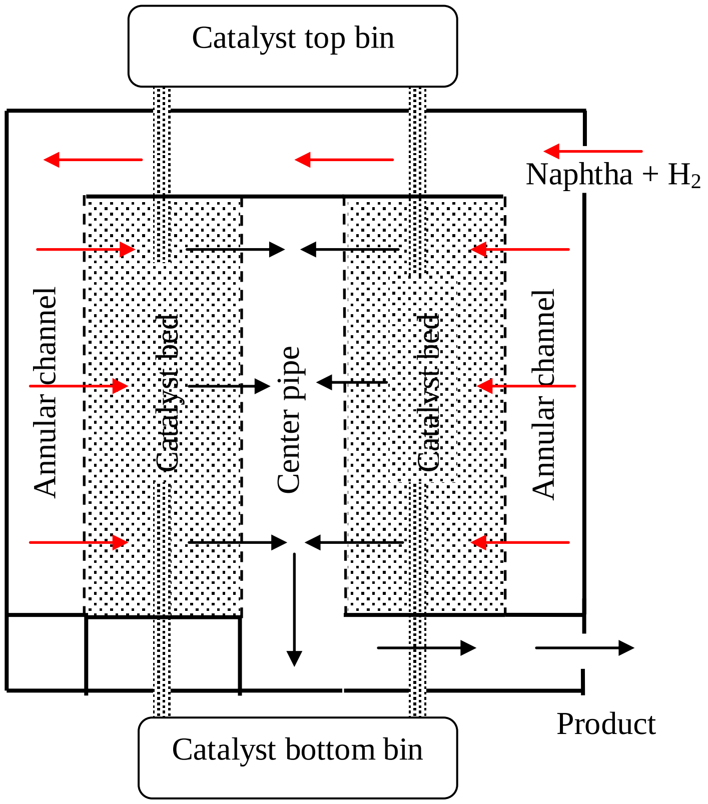

Fig. 1.4: A diagram of radial flow moving bed reactor (RFMBR).

1.4 Problem Statement

In a petroleum refinery, naphtha is reformed in a RFMBR (Radial Flow Moving Bed Reactor) to produce aromatics and hydrogen. A parallel (unwanted) hydro-cracking reaction may also convert naphtha to light gases with consumption of hydrogen. Very little is known in the open literature about the performance of naphtha reforming in a RFMBR to help in analyzing strategies to minimize hydro-cracking reactions. Performance of the RFMBR is dependent on the characteristics of catalyst, reaction rate constants, catalyst decay rate constants, gas velocity, particle velocity, pinning and particle attrition. Quantitative model to estimate conversions and yields incorporating the various factors affecting naphtha reforming in a RFMBR is needed to help in analyzing ways and means of reducing the parallel hydro-cracking reactions. Simple models to explain the phenomena of pinning and attrition are needed to reduce their impact on reactor performance. In this thesis, an attempt is made to develop these models and suggest strategies to improve production of aromatics and hydrogen while reducing production of light gases.

1.5 Objectives

Followings are the main objectives of the project:

- To develop a heterogeneous gas-solid catalytic reactor model to represent the operation of naphtha reforming in radial flow moving bed reactor (RFMBR).
- To simulate and investigate the sensitivity of the model with various parameters.
- To develop simple models to explain the phenomena of pinning and attrition.
- To explore strategies to minimize production of light gases and improve the production of aromatics and hydrogen.

1.6 Scope of the Study

Naphtha reforming process is a matured technology and there is constant endeavor to improve the catalysts, reactors, regenerators and operating strategies to maximize aromatics and hydrogen production while reducing light gas production.

This work aims at developing a model to describe the performance of naphtha reforming in a radial flow moving bed reactor. The model will be used to simulate and investigate ways and means of improving the productivity of the reformer This work also aims at developing simple models to explain the phenomena of pinning and attrition.